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INFORMATION BRIEF

Title: On-line Coolant Chemistry Analysis

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Summary: Impurities in the gas coolant of the space nuclear power plant (SNPP) can provide valuable indications of problems in the reactor and an overall view of system health. By monitoring the types and amounts of these impurities, much can be implied regarding the status of the reactor plant. However, a preliminary understanding of the expected impurities is important before evaluating prospective detection and monitoring systems. Currently, a spectroscopy system is judged to hold the greatest promise for monitoring the impurities of interest in the coolant because it minimizes the number of entry and exit points to the plant and provides the ability to detect impurities down to the 1 ppm level.

Introduction: The gas coolant selected for use in the Project Prometheus SNPP is comprised of approximately 72 volume percent helium and 28 volume percent xenon. Inevitably, impurities will contaminate the coolant. Impurity species can arise from outgassing of the structural materials and gas-solid reactions with water vapor and other adsorbed species in the system prior to filling, as well as volatilization of high vapor pressure elements such as iron, nickel and chromium found in nickel-based superalloys and movement of interstitial atoms, like oxygen, nitrogen and carbon, through the system. The impurities and structural materials will not react with the bulk coolant gas since it is inert. Impurities will react with one another as well as the reactor structural materials, establishing a complex equilibrium (or quasi-equilibrium) condition, and could adversely affect the performance and lifetime of the SNPP by accelerating corrosion and degrading the mechanical properties in all structural materials. Not all impurities will adversely impact the structural materials. Active impurity controls might prevent the decarburization of superalloys by maintaining critical trace levels of carbon and/or oxygen in the system. However, the gas composition would be indicative of the overall health and function of the system, and would provide verification of the performance of active control systems. For example, the presence of fission products would signify a problem in the fuel system, while higher than usual levels of carbon-bearing species, e. g., CO or CH_4, might indicate decarburization of superalloys or loss of passification of silicon carbide components.

Before evaluating the analytical methods that might be considered for use in the gas monitoring system, consideration must be given to the gas temperature and the partial pressures of the impurities of interest with regard to the varying temperature and pressure conditions throughout the plant. If a sampling system were used to transport the gas from the plant to the analysis system, the sample may be altered if some constituents condense in the sampling apparatus before reaching the monitoring system. Also, the amount of gas coolant present in the reactor is limited, so a monitoring technique that returns the sample to the system unaltered would be preferred over a

system that alters the sample during testing or requires the sample to be exhausted from the system.

To choose the candidate detection methods, the contaminants of concern must first be identified because different types of analytical systems have varying capabilities and sensitivity for detection of specific elements and compounds. Thermochemical modeling development was initiated to provide a capability for preliminary identification of potential contaminants. The gas velocities in the plant were estimated to be of the order of 100 meters-s^{-1}, meaning that one pass through the system would occur in a timeframe on the order of seconds. Since the gas coolant will complete a loop through the reactor so quickly, the gas would likely not achieve thermodynamic equilibrium with the wall and structural materials at all points in the system. However, equilibrium thermodynamic modeling provides reasonable predictions of potential contaminants and their expected concentration levels. Assuming that operating windows for chemistry factors, such as oxygen potential and carbon potential, can be identified, maintenance of impurity levels within specified limits may necessitate the use of an active or passive chemistry control system, and analytical methods would be required with capability to assess the critical constituents at levels consistent with the prescribed operating limits.

Modeling: Before evaluating analytical techniques and sampling systems, modeling was used to identify the potential contaminants of concern. Many detection systems can only identify particular atoms and molecules, so it is important to know the impurities of interest before choosing a particular type of monitoring system.

Published literature on the measured level of initial impurity concentrations in high temperature gas reactors (HTGRs) are listed in Table 1 below [1], [2].

Table 1 -- Impurities in High Temperature Gas Reactors

Impurity	Concentration (ppm)
H_2	500
H_2O	1.5
CO	15
CH_4	20
N_2	<5
O_2	<1

The levels of carbon-containing impurities given are typical of HTGR's with graphite cores and/or significant amounts of silicon carbide structures. Lower carbon potentials are expected in the SNPP, except possibly in the case of use of SiC structural materials in the core.

Hall evaluated the atmosphere of a preconceptual SNPP [3] with an equilibrium thermodynamic model using HSC Chemistry [4] to estimate impurity levels, considering only the highest temperature application for the superalloys, 1150K in the turbine, and fuel cladding temperatures of 1400K for the refractory metals and silicon carbide. The model assumes that water is the only impurity initially present in the HeXe coolant. All

other impurities are accounted for as products yielded from a reaction between water and constituents of the structural materials, specifically chromium carbides in the superalloys. Comparable assumptions predicted the impurity levels reported for HTGR's with reasonable accuracy, lending credibility to the argument that the model was a reasonable first approximation of the space nuclear power plant environment. With this model, Hall found that the impurity levels vary with the temperature of the system and that the initial amount of water in the system determines the balance between oxidation and carburization potentials. These two factors, along with temperature, were noted to govern the critical effects on superalloys, refractory metal alloys and silicon carbide with regard to oxidation, carburization and decarburization.

At this time, there were two combinations of structural materials under consideration for use in the SNPP: (1) nickel-base superalloys (NBSAs) with refractory metal alloy core structurals, and (2) NBSAs with silicon carbide core structurals. All NBSAs under consideration were chromia formers.

Hall's analysis focused on the condition of the structural materials, namely retention of a chromia film on the superalloys, decarburization of the superalloys by decomposition of chromium carbide, and formation of the oxides of the refractory metals. The specific constituents and partial pressures of the impurity species in the gas were not explicitly evaluated.

A second, similar model was created based on comparable assumptions using FactSAGE™ [5], another thermodynamic modeling program using the following reactions:

$$He + SiC + Cr_2O_3 + H_2O, \quad (1)$$

and

$$He + Mo + Cr_2O_3 + H_2O, \quad (2)$$

with water as the limiting reactant. Refractory metals will not passivate in an oxidizing environment. NBSAs will form a protective oxide on the surface in a sufficiently oxidizing environment. Chromia was used to represent the NBSA in the model while a representative, unalloyed refractory metal, molybdenum, is used.

FACTSage's results are based on thermodynamic equilibrium only and do not account for reaction kinetics. Unlike Hall's model, the temperature and pressure are fixed in this analysis. However, the extreme high and low gas temperatures predicted for the SNPP were used and pressure was included explicitly corresponding to the system state points for the gas cooler and the turbine inlet, respectively: 350K at 10.1 kPa pressure, and 1150K at 19.1 kPa pressure. The constituents of the gas and their concentrations were calculated for each material combination at each condition. The results are provided in Tables 2 and 3.

Table 2 -- Gas Constituents and Concentrations Predicted in the Space Nuclear Power Plant for SiC + Cr_2O_3

High Temp. & Pres. (1150 K and 19.1 kPa)		Low Temp. & Pres. (350 K and 10.1 kPa)	
Impurity	**Volume Percent**	**Impurity**	**Volume Percent**
He	0.998561	He	100
CO	0.000736	CH_4	0.000124
H_2	2.59E-06	H_2	1.19E-05
CO_2	4.21E-07	H_2O	2.84E-20
H_2O	1.74E-09	C_2H_4	3.29E-22
CH_4	3.02E-12	CO	5.86E-27
SiO	2.21E-13		
C_2H_2	1.2E-13		

Table 3 -- Gas Constituents and Concentration Predicted in the Space Nuclear Power Plant for Molybdenum + Cr_2O_3

High Temp. & Pres. (1150 K and 19.1 kPa)		Low Temp. & Pres. (350 K and 10.1 kPa)	
Impurity	**Volume Percent**	**Impurity**	**Volume Percent**
He	100	He	100
H_2	0.000167	H_2	0.00026
H_2O	9.33E-05	H_2O	1.6E-09
MoO_3	0.55377E-12		
O_2	0.29699E-16		

As expected, the concentration of impurities increases with temperature and pressure for both materials combinations. This analysis of impurity concentrations provides a basis for evaluation of gas chemistry monitoring systems.

Monitoring System

1. Requirements for the System

The gas temperatures in the SNPP range from 390 to1150K while pressures vary between 10.1 and 19.2 kPa. This creates a large differential that the coolant will pass through in a period of several seconds. The monitoring system will need to withstand temperatures and pressures consistent with the location of access points for required sensors or windows. Also, given the limited amount of coolant initially in the system, even infinitesimal coolant leakage could adversely impact the system performance. Careful consideration and development of reliable interfaces would be required for any monitoring sensors or windows. Ideally, analysis of the gas would be performed in-situ via a method such as spectroscopy, precluding the need for removal of gas to a remote location. A method such as spectroscopy could significantly reduce the concerns for impurity condensation in the sampling system, as well as eliminating the gas loss potentially associated with a remotely located system.

2. Past Systems

The issue of monitoring the coolant in a gas cooled reactor is not new. National Aeronautics and Space Administration (NASA) and Department of Energy (DOE) projects previously have addressed this issue.

Workers at Battelle Northwest Laboratory developed an infrared hygrometer for monitoring the gas coolant in a terrestrial reactor [6]. The monitoring system was used to detect leaks in the coolant system, as well as to monitor material corrosion rates. The system monitored water vapor levels between 20 and 10,000 ppm at standard temperature and pressure, and was more sensitive at higher temperatures and pressures; at 590K (600°F) and 300 psia, the hygrometer could detect water vapor levels between 2 and 1000 ppm.

The infrared hygrometer can detect other impurities by modifying the spectral range of the detector. Absorption bands of other species may interfere with IR hygrometry measurements in the case of complex mixtures. The largest absorption peak should be selected for each impurity to maximize sensitivity. The optimum peaks for water and carbon dioxide are 2.6 μ and 2.7 μ, respectively. Detecting water and carbon dioxide will necessitate a trade-off in sensitivity between the two. However, IR absorption could prove useful because it can detect a wide range of elements.

The absorption hygrometer passed infrared radiation through the flowing gas and measured the loss of energy in the absorption band of interest. In the Battelle work, an IR transparent quartz window was used. Previously, Battelle used Corning 2550 glass.

Development of a Fourier Transform Infrared (FTIR)-based spectroscopy system has also been reported and used to monitor 30 trace gases on manned spacecraft [7]. FTIR was chosen for its accuracy and speed. The gas concentrations were measured relative to spacecraft maximum allowable concentrations, known as SMAC values. Depending on the species, SMAC values are of the order of parts per million to parts per billion concentrations. Thus excellent sensitivity is demonstrated for specific species.

More recently, several European companies developed the Analyzing Interferometer for Ambient Air (ANITA) for the ESA as a gas analyzer for use in monitoring manned spaces on the International Space Station [8]. The system was designed to run for 10 days, but could operate up to 6 months. The ESA expects ANITA to serve as the forerunner for a permanent gas monitoring system on the International Space Station.

ANITA uses infrared absorption spectroscopy to detect 32 critical gases to ppm and sub-ppm levels within three to four minutes. The detectable gases have absorption peaks in the infrared region, between 600 and 5000 cm^{-1}, and the analysis was noted to be non-destructive.

NASA developed the Hazardous Gas Detection System (HGDS) to detect leaks in the cryogenic fuel system of the Space Shuttle [9]. The cryogenic fuel is liquid hydrogen. The HGDS detects hydrogen, helium, nitrogen, oxygen and argon down to levels of 1 ppm with a quadrupole mass spectrometer. An important feature of the HGDS is its ability to expand its range and detect additional gases that may be of future interest.

This flexibility ensures that the system remains useful and applicable in numerous applications. Sampling lines deliver gas from several locations of interest into one mass spectrometer system. The lines were Tygon tubing, which allowed ambient air and water to diffuse through. This made it difficult to accurately measure constituents of air down to the low ppm level. Measurements times are only 10 seconds and an additional 20 seconds is required to recover to make the next measurement.

3. Commercially Available Systems

There are numerous commercially available methods for monitoring gases. These techniques were reviewed for their applicability to the requirements of impurity detection in the space nuclear power plant.

3.1 Gas Chromatography

Gas chromatography (GC) separates a gaseous sample by passing it through a filled column. The sample is carried through by an inert gas moving at a higher velocity than the sample. The sample combined with the inert gas is referred to as the mobile phase. The stationary phase is the solid filler in the column, usually a high surface area material such as carbon or diatomaceous earth, coated with a liquid that has a specific affinity for the gaseous impurities of interest. The attraction between the different components of the sample and the absorbing liquid retards the species movement through the column thus effecting separation of the impurities. The individual species must then be passed through an appropriate detector to identify the species and quantify the amount of each [10].

As the column in a gas chromatograph increases in length, each species is more definitively separated. However, GC is not capable of specifically identifying gas species, only separating them. Various detectors are capable of identifying different molecules. Thus, the capabilities of gas chromatography are dependent on the detector used. Some popular detectors are identified in Table 4.

Table 4 -- Detectors Used in Gas Chromatography

Detector	Capabilities	Comments
Flame Ionization Detector (FID)	Sulfur down to 200 ppb Phosphorus down to 10 ppb	Sample is destroyed.
Helium Ionization Detector (HID)	Volatile inorganics (NO_x, CO, CO_2, O_2, N_2, H_2S, and H_2) down to low ppm range	There is no filament to burn out
Photo Ionization Detector (PID)	All molecules with an ionization potential <10.6 eV (This includes aromatics and molecules with double bonds, such as unsaturated hydrocarbons.)	Non-destructive test
Reduction Gas Detector (RGD)	Most sensitive to H, CO and other reducing gases to low ppb for H and ppt for CO	

Detector	Capabilities	Comments
Dry Electrolytic Conductivity Detector (DELCD)	Sensitive to chlorinated and brominated compounds to low ppb range Combined with FID allows identification of hydrocarbons to ppm range	
Thermal Conductivity Detector (TCD)	Most universal detector to (0.01 to 100%) 100-1,000,000 ppm	
Catalytic Combustion Detector (CCD)	Detects hydrocarbons	
Atomic Emission Detector	Can monitor emitted radiation from 170-78 nm (N, P, S, C, Si, Hg, Br, Cl, H, etc.)	

As shown in Table 4, the effect of testing on the sample depends on the detector. GC can detect a broad range of gases through the use of multiple detectors, but the arrangement of a GC column and multiple detectors, as well as limited detector lifetime may be an issue. Some manufacturers of gas chromatography systems are Shimadzu Scientific Instruments, OI Corporation, Siemen Process Analytics, and SRI Instruments.

3.2 Mass Spectroscopy

Mass spectroscopy systems identify molecules according to their mass-to-charge ratios. Unlike gas chromatography, mass spectroscopy systems can identify compounds but is unable to separate them [10]. There are three common types of mass analyzers described below: quadrupole, time of flight and double focusing.

Quadrupole mass analyzers are the most popular analyzer in mass spectroscopy systems. Such systems have a mass resolution of 0.1 to 0.2 amu and mass-to-charge ratios up to 4,000 can be detected.

For time of flight mass spectrometers, positive ions are produced by hitting the sample with electron pulses. The ions then enter a 1 meter long tube where the ions with higher mass-to-charge ratios will take longer to travel through. The ions are detected at the end of the tube. The results from time of flight spectrometers are not as reproducible or accurate as quadrupole and magnetic separators. However, some benefits are derived from the system's simplicity: It is rugged and offers easy access to the sample and can detect over an unlimited mass-to-charge ratio range.

In double focusing mass spectrometers, two beam focusing devices are employed: an electrostatic analyzer and a magnetic sector analyzer. Ions from the source accelerate through a slit into a curved electrostatic field that focuses a beam of ions with a narrow range of kinetic energies into another slit that leads into a region with an applied magnetic field. In the magnetic field, the ions deflect according to their mass-to-charge ratio and then impinge on a photodetector.

Mass spectroscopy is applicable to a wide range of gases but may alter the sample composition, due to selective sampling.

3.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) detects changes in vibrational energy within a molecule when it is excited by an infrared signal. FTIR normally operates in the region of the electromagnetic spectrum between 14,000 and 400 cm^{-1}. The far infrared region (400 to 10 cm^{-1}) is particularly useful for detecting molecules which contain inorganics [10]. The IR spectrum of each species, elementary or compound, is unique and a computer program is used to identify the species based on the observed spectrum.

Use of FTIR requires an infrared transparent window, frequently potassium bromide, sodium chloride, or fluorite. Since the analysis is performed through the window, the sample does not leave the system and is not affected by the analysis. Given the limited amount of gas coolant in the system, this makes FTIR very appealing. However, the window material could be problematical, depending upon its temperature capabilities and chemical stability. In addition, the window would require mounting to the system, representing a penetration through the pressure boundary, and a potential leak.

FTIR is fast and can identify some functional groups as well as inorganic gases to the ppm level. However, such systems cannot detect diatomic molecules, water, metals or ionic salts.

The MIDAC Corporation manufactures industrial FTIR systems that are able to withstand the anticipated pressures and temperatures of the SNPP. Other manufacturers include MKS Instruments, the Thermo Electron Corporation, and Pace Analytical Services.

3.4 Raman Spectroscopy

Raman spectroscopy monitors the vibrational energy changes of inelastically scattered photons [10]. In order to detect these photons, the polarizability (α) must vary with the orientation of the molecules.

Raman spectroscopy is useful for detection of molecules that do not have a permanent dipole moment, and are not detectable by IR spectroscopy. An intense source of monochromatic light (a laser) is required for excitation and ambient light must be minimized. Although Raman cannot detect water, its presence does not impede measurement of other species. However, Raman spectroscopy is not sensitive down to the ppm level.

Recommendations:

An FTIR system appears to be the most capable for use in monitoring the gas in the SNPP. This is largely because the sample does not need to be removed from the system for analysis. In addition, FTIR is sensitive enough to detect impurities down to the 1 ppm level. However, FTIR is not able to detect all impurity species of interest, including diatomic molecules, and, depending upon the species required to be analyzed, the FTIR system could need to be coupled with another technique.

The MIDAC Corporation manufactures FTIR systems for industrial applications. Informal discussions indicated that their systems could withstand the temperature and pressure

requirements of the SNPP. An estimated cost is $165,000 for the FTIR system only; this does not include parts necessary for installation and interface to the plant.

Despite its advantages, implementing the spectroscopy system into the plant will require significant engineering development. Spectroscopy is advantageous because it does not require removing gas from the system; however, the IR beam must have access to the system through an infrared transparent window. This window presents substantial challenges. It must withstand the temperature and pressure of the system, as well maintain a leak tight seal despite thermal cycling and, possibly, pressure fluctuations. In addition, the window must be chemically inert, and neither be affected by, nor have any effect on, the system gas chemistry.

If an FTIR system were used in the flight system, a significant volume and weight penalty may accrue. Additionally, the instrumentation would require shielding from radiation and structural damage from debris. The window would require special attention due to its inherently brittle nature, and would have to be located in an area where radiation damage would not affect its optical properties. Remote location of the instrumentation could potentially be effected by the use of fiber optics.

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